Synthesis and reactivity of dichloroboryl complexes of platinum(II)

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The reaction between \([\text{Pt}(\text{nbe})_3]\) (nbe = norbornene), two equivalents of the phosphines PPh₃, PMePh₂ or PMe₃-Ph and 1 equivalent of BCl₃ affords the platinum dichloroboryl species \([\text{PtCl}(\text{BCl}_2)(\text{PPh}_3)_2]\), \([\text{PtCl}(\text{BCl}_2)(\text{PMePh}_2)_2]\) and \([\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]\). All three complexes were characterised by X-ray crystallography and reveal that the boryl group lies trans to the chloride. With PMe₃ as the phosphine, the complex \([\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]\) is isolated in high yield as a white crystalline powder although crystals suitable for X-ray crystallography were not obtained. Crystals were obtained of a product shown by X-ray crystallography to be the unusual dinuclear species \([\text{Pt}_2(\text{BCl}_2)_2(\text{PMe}_3)_4]\) trans to the chloride. With PMe₃ as the phosphine, the complex \([\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]\) is isolated in high yield as a white crystalline powder although crystals

Introduction

Transition metal boryl compounds¹ remain a focus of continued interest not least because of their involvement in various metal catalysed diboration and other borylation reactions.² In most examples, the boron of the boryl ligand is bonded to a single metal centre and two additional atoms which are usually good π-donors such as oxygen or nitrogen incorporated into diolato or amido groups respectively; the B(cat) group, where cat = catecholate, is one of the most studied.³ More recent investigations, notably by Braunischweig et al. and Aldridge et al., have focussed on more reactive boryl species in which the R groups of the BR₂ ligand are hydrocarbyl and/or halogeno groups.

With particular reference to dihaloboryl ligands, BX₂ (X = F, Cl, Br, I), the earliest examples were reported by Nöth and Schmid in the 1960’s.⁴ Thus in a series of papers, reviewed in ref. 3, these authors described a range of dichloroboryl species including \([\text{CoCl}_3(\text{CO})_2(\text{L})]\) (L = CO, PPh₃, AsPh₃, Mn(BCl₂)(CO)(PPh₃)], [Fe(BCl₂)(CO)(η₅-C₅H₅)] and \([\text{MoCl}(\text{BCl}_2)(\text{CO})(\eta_5-C_5H_5)]\) each derived from the reaction between BCl₃ and the corresponding metal carbonylate anion. Alternatively, dihaloboryl species were reportedly formed via B–X bond (X = halide) oxidative addition to Pt(0) or Co(0) centres, examples being the Pt(0) species \([\text{PtBr}(\text{BrB}_2)(\text{PPh}_3)_2]\) and the Co(0), formally 19-electron, complexes \([\text{CoX}(\text{BX}_2)_2(\text{dppe})_2]\) (X = Cl, Br, I; dppe = 1,2-bis(diphenylphosphino)ethane),⁵,⁶ both proposed to have a cis configuration. The bis-boryl, 19-electron Co(0) complexes trans-\([\text{Co}(\text{BX}_2)_2(\text{dppe})_2]\) (X = Br, I) were also described, derived from the reaction between \([\text{CoH}(\text{dppe})_2]\) and BX₂,⁷,⁸ These latter complexes were reported to be particularly versatile boryl transfer agents, the complex trans-\([\text{CoBr}_2(\text{dppe}_2)]\) being used to synthesise complexes of rhodium, copper and silver containing the BR₂ ligand.⁹,¹⁰ Nevertheless, despite the impressive number of reports, none of these early compounds were structurally characterised and, partly on the basis of the ¹¹B NMR data presented, some doubt remains as to their correct formulation.

More recent work has provided the first definitive characterisation of dihaloboryl species. Thus, the first structurally characterised BF₂ complexes cis-\([\text{Pt}(\text{BF}_2)_2(\text{PPh}_3)_2]\), \([\text{Pt}(\text{BF}_2)_2(\text{dppe})_2]\) (dppe = 1,2-bis(diphenylphosphino)butane) and \([\text{Ir}(\text{BF}_2)_3(\text{CO})(\text{PPh}_3)_2]\) were recently described by us derived from the oxidative addition of BF₃ to Pt(0) and Ir(0) precursors respectively;¹¹ spectroscopic data for an iridium BF₂ complex \([\text{Ir}(\text{BF}_2)_2(\text{PMe}_3)_2(\eta_5-C_5\text{Me}_5)]\) had previously been reported by Bergman and co-workers.⁷ In 2000, the osmium dichloroboryl complex \([\text{OsCl}(\text{BCl}_2)(\text{CO})(\text{PPh}_3)_2]\) had previously been reported by Roper et al. having been prepared from the reaction between \([\text{OsCl}(\text{Ph})(\text{CO})(\text{PPh}_3)_2]\) and HBCl₃·Et₂O.¹² This and a number of subsequent reports revealed a rich chemistry of the BC₁ ligand involving substitution at boron and resulting in a range of new boryl, tethered boryl and base-stabilised borylene complexes of osmium.¹³,¹⁴ More recently, Braunischweig and...
co-workers have presented structural data for [Fe(BCl3)(CO)2(n- 
C5H5)] (δB 90.0), the first dichloroboryl complex to be structurally 
characterised.20 These authors also reported the structure of the 4- 
picoline adduct [FeCl(B(4-pic))(CO)2(n-C5H5)] (δB 18.8) in which 
the nitrogen atom is directly bonded to the boron centre.20 In later 
reports, Braunschweig and co-workers have described the analog-
uous pentamethycyclopentadienyl complexes [FeCl2(BCl3)(η- 
C5Me5)] (δB 94.9)11 and [Fe(BBr2)(CO)2(η-C5Me5)] (δB 94),14 the 
former affording, on reaction with [Pd(PCy3)2], the heteronuclear 
complex [(η-C5Me5)Fe(μ-CO)(μ-BCl2)Pd(PCy3)] (δB 72.2) contain-
ing a bridging dichloroboryl ligand.11 Spectroscopic data were 
also presented for the phosphine adduct [Fe2Cl2(PCy3)(η- 
C5Me5)] (δB 3.4).15 Both the cyclopentadienyl and pentamethyl-
cyclopentadienyl iron dichloroboryl compounds have also been 
employed as precursors in the synthesis of dinuclear species 
containing substituent-free bridging boron atoms.15

In most of the recent studies, and much of the early work 
reported by Nöth and Schmid, the dihaloboryl species were 
prepared from a reaction between a boron trihalide and an anionic 
transition metal complex. The exceptions to this method involved 
an oxidative addition reaction either of a B–B bond, in the case 
of the BF2 complexes,6 or of a boron–halogen bond in the case 
of some of the platinum and cobalt complexes described by Nöth 
and Schmid.1 In view of the known facile oxidative addition of 
B–X bonds to Pt(0), exemplified by the synthesis of such com-
plexes as [PtCl2(B(cat)) (PPh3)2],16 [PtCl2(B(NMe2)2)2(PPh3)2],17 
and [PtBr2(BBr3)(PCy3)] (Pc = ferroceny1,18 Cy = cyclohexyl)18 
from ClB(cat), 1,2-B2Cl2(NMe2)2 and BBr2(Fc) respectively, we 
were interested in establishing whether dihaloboryl compounds 
could be accessed directly from Pt(0) precursors and boron 
trihalides. Herein we describe the results of these studies.

Results and discussion

We were not the first to examine the reactions between phosphine– 
Pt(0) complexes and boron trihalides. Indeed, the reaction between 
BBr3 and [Pt(PPh3)4] in cyclohexane, reported by Nöth, Schmid 
and co-workers18 and mentioned above in the Introduction, was 
purported to give the Pt(II) complex [PtBr2(BBr3)(PPh3)2]. 
However, in subsequent work by Durkin and Schram29 and later 
Wallbridge and co-workers,20 compounds formulated as Lewis 
acid–base adducts were described. Thus Durkin and Schram 
reported that treatment of solid [Pt(PPh3)4] with gaseous BCl3 
afforded the 1 : 2 adduct (Ph3P)Pt2BCl2, the same species being 
formed, along with Ph3PBCl3, when [Pt(PPh3)4] was employed.19 
This 1 : 2 adduct was apparently unstable with respect to ligand 
dissociation when dissolved in a solvent and when the reaction 
between [Pt(PPh3)4] and BCl3 was carried out in benzene solution, 
a product formulated as (Ph3P)Pt2BCl2 was proposed. In the later 
work by Wallbridge and co-workers,20 the reaction between either 
[Pt(PPh3)4] or [Pt(PPh3)2(η-C5H5)] and BF3 in toluene was reported 
to afford the adduct (Ph3P)Pt2BF3, which was shown to react with 
BCl3 to give (Ph3P)Pt2BCl3.

In this study, the reaction between [Pt(PMePh2)3] (prepared in situ 
from [Pt(nbe)3] (nbe = norborne) and four equivalents of PMePh2, 
and four equivalents of BCl3 in toluene afforded the phosphine 
adduct Me3PBCl3 (δB 86.8, 1JBB 164.7) and a platinum boryl species 
formulated as [PtCl(BCl3)(PMePh2)] (1), the 11B NMR chemical 
shift and well resolved coupling to platinum being consistent 
with the presence of a BCl3 ligand (δB 62.2, 1JBB 1214 Hz; δp 
−14.6, 1JPF 2635 Hz). Attempts to crystallise 1 from this reaction 
mixture were unsuccessful, resulting only in small quantities of 
the species [PtCl(PMePh2)][BCl3], although isolated yields of 1 as 
a white powder were typically >90%. [PtCl(PMePh2)][BCl3] was 
characterised by X-ray crystallography, details for which are given 
in Table 1.

Similar reactions employing the phosphines PPh3, PMePh2, 
PMePh3 or PCy3 (Cy = cyclohexyl) were also carried out. For PPh3, 
and PMePh3, the adducts Ph3PBCl3 and Ph3PMePh3BCl3, 
were formed (the former characterised crystallographically) 
in addition to boryl products identified spectroscopically as 
[PtCl2(PPh3)][BCl3] (2) [δB 59.8; δp 23.0, 1JPF 3023 Hz] and 
[PtCl2(PMePh2)][BCl3] (3) [δB 61.8; δp 7.6, 1JPF 2890 Hz] although in both these cases, the boryl signals in the 11B NMR were broad and no coupling to platinum was resolved.

Attempted crystallisation of 2 and 3 resulted only in the complexes 
[PtCl2(PPh3)][BCl4] and [Pt2(μ-Cl)2(PMePh2)][BCl3]; the latter 
characterised by X-ray crystallography, details for which are given in Table 1. No spectroscopic evidence was observed for platinum 
boryl complexes when reactions involving the phosphines 
PMePh3 or PCy3 were carried out, the only isolated products 
being Ph3PMePh3BCl3 and [PtCl2(μ-Cl)2(PCy3)]2, respectively, both 
identified by X-ray crystallography.

In all of the reactions carried out above, it was the tetraphos-
phine Pt(0) species, generated in situ, which was employed as 
the platinum starting material and BCl3 was added in the molar 
ratio 4B : 1Pt. These reactions were attempted in light of some 
of the earlier studies referenced above but whilst they afforded 
the desired dichloroboryl species in some cases, the products were 
difficult to isolate not least because of the presence of the co-
formed phosphine–BCl3 adducts. Reactions were therefore carried 
out in which only two equivalents of phosphine were added to the 
Pt(0) species [Pt(nbe)3] followed by one equivalent of BCl3, 
Thus reaction between [Pt(nbe)3] and two equivalents of the phosphines 
PPh3, PMePh2 or PMePh3 and one equivalent of BCl3, afforded, 
in each case, high yields of the dichloroboryl species 2, 3 and 
[PtCl(BCl3)(PMePh2)]2 (4) [δB 61.8 (br); δp −6.7, 1JPF 2731 Hz]. 
However, under similar conditions using PMe6, although 3P 
NMR spectroscopy showed the presence of 1, the solutions 
decomposed rapidly to platinum metal. When an excess of BCl3 
was used, the unusual dinuclear species 5 was formed (see below).

\[\text{PR}_3\text{Cl}\]

\[\text{Pt} \text{BCl}_2\]

\[\text{R}_3\text{Br}\]

\[\text{R}_3\text{Me}\]

\[\text{PhMe}_2\]

2, R = Ph; 3, R3 = Ph3Me; 4, R3 = PhMe2.

The complexes 2, 3 and 4 were characterised by X-ray crystallo-
graphy, the results for which are shown in Fig. 1–3; crystallographic 
data for all complexes are presented in Table 1. All three molecules 
two per asymmetric unit for 4 adopt similar structures in the 
solid state in which the boryl group is trans to the chloride, 
consistent with the known high trans influence of boryl ligands.21

The Pt–B bond distances (2, 1.972(3); 3, 1.988(3); 4, 1.963(6), 
1.971(6) Å) are all similar but markedly shorter than the Pt–B 
distance in trans-[PtCl(B(cat))(PPh3)2] (2.008(8) Å)21 although the
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|                          |
| **Formula**                | **$\text{ClBP(Ph)$_3$CH$_2$(Ph)$_3$PBCl}_3$**  | **$\text{[Pt(PMe$_3$)$_3$](dppm)}$Cl$_2$**  | **$\text{[PtCl}_2$(μ-Cl)$_2$(PC$_2$)$_2$]$^2$ PhMe$_2$PBCl$_3$** |
| $M$                        | 588.53                                       | 581.59                                      |
| Crystal system             | Monoclinic                                   | Monoclinic                                   |
| $a$/Å                      | 17.466(4)                                   | 17.466(4)                                   |
| $b$/Å                      | 11.066(2)                                   | 11.066(2)                                   |
| $c$/Å                      | 29.9175(16)                                 | 29.9175(16)                                 |
| $\beta^\circ$              | 113.81(3)                                   | 113.81(3)                                   |
| Unit cell volume/Å$^3$      | 2059.99(9)                                  | 2059.99(9)                                  |
| Space group                | $P2_1$, $Pc$                                | $P2_1$, $Pc$                                |
| $Z$                        | 4                                           | 4                                           |
| $\mu$/mm$^{-1}$            | 7.35                                        | 7.35                                        |
| Reflections                | 23631/9398/8866                             | 23631/9398/8866                             |
| measured/unique/observed$^d$ | 23631/9398/8866                             | 23631/9398/8866                             |
| $R_1$(%)                   | 2.75                                        | 2.75                                        |
| $R_1$(%)                   | 2.70                                        | 2.70                                        |
| $wR_2$(%)                  | 6.40                                        | 6.40                                        |
| Flack parameter            | −0.010(5)                                   | −0.010(5)                                   |

$^a$ Observation criterion: $I > 2\sigma(I)$. $^b$ Calculated for observed data. $^c$ Calculated for all unique data.
Fig. 1 A view of the molecular structure of compound 2. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.972(3), Pt(1)–Cl(1) 2.4368(8), Pt(1)–P(1) 2.3005(7), Pt(1)–P(2) 2.2950(7), B(1)–Cl(2) 1.791(3), B(1)–Cl(3) 1.779(3); Cl(1)–Pt(1)–B(1) 173.03(8), P(1)–Pt(1)–B(1) 173.03(8), Cl(2)–B(1)–Cl(3) 113.2(3), Pt(1)–B(1)–Cl(2) 124.9(4), Pt(1)–B(1)–Cl(3) 123.9(4); interplanar angle 81.0.

Fig. 2 A view of the molecular structure of compound 3. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.988(3), Pt(1)–Cl(1) 2.4461(8), Pt(1)–P(1) 2.2961(9), Pt(1)–P(2) 2.3005(9), B(1)–Cl(2) 1.789(3), B(1)–Cl(3) 1.757(3); Cl(1)–Pt(1)–B(1) 173.25(9), P(1)–Pt(1)–B(1) 173.51(2), Cl(2)–B(1)–Cl(3) 111.4(3), Pt(1)–B(1)–Cl(2) 125.1(4), Pt(2)–B(2)–Cl(4) 111.4(3), Pt(2)–B(2)–Cl(5) 125.1(4), Pt(2)–B(2)–Cl(6) 125.1(4); interplanar angle 92.7.

Fig. 3 A view of the molecular structure of compound 4. Selected bond length (Å) and angle (°) data include: Molecule 1 Pt(1)–B(1) 1.963(6), Pt(1)–Cl(1) 2.4385(15), Pt(1)–P(1) 2.3065(15), Pt(1)–P(2) 2.3003(15), B(1)–Cl(2) 1.794(7), B(1)–Cl(3) 1.778(7); Cl(1)–Pt(1)–B(1) 176.8(2), P(1)–Pt(1)–B(1) 176.22(5), Cl(2)–B(1)–Cl(3) 111.2(3), Pt(1)–B(1)–Cl(2) 124.9(4), Pt(1)–B(1)–Cl(3) 123.9(4); interplanar angle 85.8. Molecule 2 Pt(2)–B(2) 1.971(6), Pt(2)–Cl(4) 2.4433(15), Pt(2)–P(3) 2.3017(5), Pt(2)–P(4) 2.2994(15), B(2)–Cl(5) 1.780(7), B(2)–Cl(6) 1.782(7); Cl(4)–Pt(2)–B(2) 173.3(2), P(3)–Pt(2)–P(4) 175.46(5), Cl(5)–B(2)–Cl(6) 111.4(3), Pt(2)–B(2)–Cl(5) 124.9(4), Pt(2)–B(2)–Cl(6) 123.5(4); interplanar angle 92.8.

Pt–Cl distances are more comparable (2, 2.4368(8); 3, 2.4461(8); 4, 2.4385(15), 2.4433(15); [PtCl(B(cat))(PPh3)2] 2.4446(14) Å). In the complex trans-[PtCl(BCl(NMe2))(PPh3)2], the Pt–B and Pt–Cl distances are 2.075(10) and 2.470(2) Å, respectively, revealing that the Pt–B bond length is broadly correlated with the expected Lewis acidity of the boryl group, i.e. shorter for a more Lewis acidic boron. Each boron centre in 2, 3 and 4 is trigonal planar, the Cl–B–Cl angle being a little less than 120° and the two Pt–B–Cl angles being slightly greater (the slight asymmetry in 2 and 3 is not present in 4); a similar set of angles is observed for [Fe(BCl2)(CO)2(g-C5H5)]. In all cases, the angle between the mean platinum square plane and the mean boron trigonal plane is close to 90° (2, 81.0°; 3, 92.7°; 4, 85.8°, 92.8°) which compares with the corresponding angles for [PtCl(B(cat))(PPh3)2] (78.3°) and [PtCl(BCl(NMe2))(PPh3)2] (90.0°). We note a recent report from Marder and co-workers describing DFT studies on Pt(II) boryl species of the type [PtCl(BR2)(PMe3)2]. The trends observed experimentally in the Pt–B and Pt–Cl bond lengths are in full accord with those predicted by the DFT calculations. Thus the trans influence of the B(cat) and BCl1 groups was calculated to be nearly identical, whilst shorter Pt–B distances were anticipated for Pt–BCl1 (1.976 Å) vs Pt–B(cat) (2.005 Å). 

Reactions involving the diphosphines dppe (1,2-bis(diphenylphosphino)ethane) and dppm (bis(diphenylphosphino)methane) were also carried out. Thus reaction between [Pt2(dppm)3] and BCl3 afforded a mixture of products, one of which was shown by X-ray crystallography to be the dppm–BCl3 adduct Cl3BP(Ph)2CH2(Ph)2PBCl3, details of which are given in Table 1.
Crystals of the unusual dinuclear species \([\text{Pt}_2(\text{BCl}_2)(\text{PMe}_3)_4(\mu-\text{Cl})][\text{BCl}_4](5)\) were obtained. A view of the structure of the cation is shown in Fig. 4 which reveals an arrangement in which two square planar platinum(II) centres are linked by a single bridging chloride which is trans to a BCl₂ group on each platinum centre. Both Pt–B bonds [1.960(5) and 1.955(4) Å] are similar in length to those observed for 2, 3 and 4 as are the Pt–Cl bond lengths [2.5155(10) and 2.5088(11) Å]; the boron trigonal planes are also close to orthogonal with respect to the platinum square planes (89.4 and 86.3°). Whilst the mechanism by which compound 5 is formed is unclear, a formal equation for its formation, eqn (1), is consistent with the expected high trans influence of the boryl groups resulting in the lability of a trans chloride which is subsequently scavenged by BCl₃.

\[
2\text{[PtCl}(\text{BCl}_2)(\text{PMe}_3)_2\text{]} + \text{BCl}_3 \rightarrow \text{[Pt}_2(\text{BCl}_2)(\text{PMe}_3)_4(\mu-\text{Cl})][\text{BCl}_4] \tag{1}
\]

Having a reliable route to quantities of \([\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]\) (1), enabled a study of its reactivity to be carried out which is summarised in Scheme 1. Thus treatment of 1 with NEt₃ or pyridine (py) afforded the adducts \([\text{PtCl}(\text{BCl}_2)(\text{NEt}_3)(\text{PMe}_3)_2]\) (6) \(\delta_B 27.8; \delta_P -13.0; J_{\text{PtP}} 2643 \text{ Hz} \) and \([\text{PtCl}(\text{BCl}_2)(\text{py})(\text{PMe}_3)_2]\) (7) \(\delta_B 29.9; J_{\text{PtPy}} 957; \delta_P -10.4; J_{\text{PtP}} 2694 \text{ Hz} \) respectively, both characterised spectroscopically. Proposed structures for 6 and 7 are shown in the diagrams below consistent both with the \(^{11}\text{B} \) NMR data and the known structure of the species \([\text{Fe}(\text{BCl}_2(4-\text{pic}))\{(\text{CO})_2(\mu-\text{C}_5\text{H}_5)\}]\). Treatment of 1 with dppm afforded a mixture of products of which only the salt \([\text{Pt}(\text{PMe}_3)_2(\text{dppm})\text{Cl}_2]\) was characterised; X-ray crystallographic data for this species are given in the Experimental section.
The reaction between 1 and either four equivalents of NHEt₂ or piperidine (pipH) resulted in the mono-substituted boryl species trans-[PtCl₂(BCl(NHEt₂))(PMe₃)₂] (8) (δₚ 35.9, JₚPtB 1028; δₓ 13.1, JₓPtB 2772 Hz) and [PtCl₂(BCl(pip))(PMe₃)₂] (9) (δₚ 34.3; δₓ 9.9, JₓPtP 3000 Hz) respectively, the eliminated HCl in each case removed as [NH₂Et₂]Cl or [pipH₂]Cl. Even with sufficient diethylamine or piperidine present, no evidence was obtained for a disubstituted boryl species. Spectroscopic data for 8 and 9 were consistent with the proposed structures and compound 8 was also characterised by X-ray crystallography, the results of which are shown in Fig. 5. The structure of 8 is similar to those of 2, 3 and 4 described above. Notable differences, however, are the longer Pt–B and Pt–Cl bond lengths [2.005(4) and 2.4604(10) Å respectively], the former a likely consequence of the less Lewis acidic boron centre resulting from the π-donor diethylamido substituent as described earlier. The angle between the platinum mean square plane and the boron mean trigonal plane is 90.0° and that between the adjacent boron and nitrogen trigonal planes is 6.0° (consistent with the π-donor properties of the amido nitrogen). In all respects, the structure of 8 is similar to that previously reported for the dimethylamido analogue trans-[PtCl₂(BCl(NMe₂))(PPh₃)₂].

Treatment of either 1 (in the presence of excess NHEt₂) or 8 with catechol afforded the B(cat) derivative trans-[PtCl₂(B(cat))(PMe₃)₂] (10) (Schemes 1 and 2) characterised spectroscopically (δₚ 33.3, JₚPtB 1039; δₓ 12.6, JₓPtP 2768 Hz) and by X-ray crystallography. The results of the structure determination are shown in Fig. 6 and reveal the expected trans geometry as observed for related species including the chloro–B(cat) complex trans-[PtCl₂(B(cat))(PPh₃)₂]. As shown in Scheme 2, complex 10 was formed in the reaction between [Pt(PMe₃)₄] and ClB(cat) and also from the slow decomposition of cis-[Pt{B(cat)}₂(PMe₃)₂] (11) in dichloromethane over a period of months. Compound 11 (δₚ 49.4; δₓ 14.3, JₓPtP 1490 Hz) was prepared from the reaction between [Pt(PMe₃)₄] and B₂(cat), by analogy with other Pt(II) bis-boryl species, and is structurally similar (Fig. 7) to all related bis-phosphine, platinum(II) bis-boryl species.
In conclusion, these studies have shown that platinum(II) dichloroboryl complexes of the form $\text{trans-[PtCl(BCl)](PR)}_2$ can be formed in high yield from the oxidative addition of a B–Cl bond in BCl$_3$ to a platinum(0) centre in the presence of two equivalents of a phosphine ligand. Furthermore, an examination of the reactivity of such species, $\text{trans-[PtCl(BCl)](PMe)}_3$, in particular, reveals an adduct chemistry associated with the Lewis acidic boron centre, consistent with the previous work of Braunschweig and a substitution chemistry of the B–Cl bond(s) which parallels the chemistry observed by Roper for the related osmium BCl$_3$ complex described in the Introduction. The original report by Nöth and Schmid of oxidative addition of BB$_3$ to Pt(0) resulting in a BB$_3$ ligand is therefore consistent with these studies. In contrast, however, we obtained no evidence for BCl$_3$ adducts of platinum(0) as described by Schram and later Wallbridge.

**Experimental**

**General procedures**

All reactions were performed under dry dinitrogen using standard Schlenk line techniques. Dry solvents were obtained from an anhydrous engineering system and were degassed prior to use. All reagents were procured commercially and used without further purification except for [Pt(nbe)$_3$]$_2$ (nbe = norbornene = bicyclo[2.2.1]heptene) and B$_2$(cat)$_2$. which were prepared by literature methods.

**Preparations**

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\text{[PtCl(BCl)](PMe)}_3 \] (1). [Pt(nbe)$_3$] (0.10 g, 0.21 mmol) was dissolved in hexane (5 cm$^3$), to which PMe$_3$ (0.099 cm$^3$, 0.84 mmol) was added through a micro-syringe. The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo to give a white solid. The solid was dissolved in toluene (10 cm$^3$), and BCl$_3$ (0.84 cm$^3$, 0.84 mmol, 1 M in heptane) was added at $-78$ °C. The mixture was allowed to warm to room temperature, and stirred for 1 h during which time a quantity of white precipitate formed. After this time, all volatiles were removed in vacuo, and the solid was redissolved in toluene (10 cm$^3$) and filtered, affording a colourless solution which was allowed to stand overnight resulting in a further precipitate of the by-product, Me$_3$PBCl$_3$. The solvent was removed slowly in vacuo, and the resulting solid redissolved in toluene (5 cm$^3$), and filtered to produce a solution of 1 from which a white powder was obtained after further solvent removal (0.096 g, 97%). Spectroscopic data for 1: NMR (CD$_2$Cl$_2$) $^1$H 7.66–7.73 (m), 7.33–7.41 (m), 7.23–7.28 (d), 6.65 (s), 2.30 (t, $J_{PP}$ 2635 Hz); 1H 12.1 (s), 130.6 (s), 128.3 (s), 125.3 (s); interplanar angles 81.4 [B(1)], 91.5 [B(2)].

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\text{[PtCl(BCl)](PPh)}_3 \] (2). [Pt(nbe)$_3$] (0.20 g, 0.42 mmol) and PPh$_3$ (0.22 g, 0.84 mmol) were dissolved in toluene (5 cm$^3$) and the reaction mixture stirred for 1 h, after which time the species were identified as [PtCl(PMe$_3$)$_3$][BCl$_4$] by X-ray crystallography.
[PtCl(BCl2)(PMePh2)](3). [Pt(nbe)](0.10 g, 0.21 mmol) and PMePh2 (0.080 cm3, 0.42 mmol) were dissolved in toluene (5 cm3) and the reaction mixture was stirred for 1 h, after which time the solvent was removed in vacuo to give an off-white oil. This oil was then dissolved in toluene (5 cm3), and BCl3 (0.21 cm3, 0.21 mmol, 1 M in heptane) was added at −78 °C. The mixture was allowed to warm to room temperature, and stirred for 1 h. All volatiles were then removed in vacuo, and the resulting solid was redissolved in toluene (3 cm3) and filtered. The filtrate was evaporated in vacuo to give a white solid (0.085 g, 57%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (1 cm3) layered with hexane. Spectroscopic data for 3: NMR (CDCl3) 1H δ 61.8 (br), 31P[H] δ −6.7 (Jref 2731 Hz), 13C[1H] δ 131.3 (t, Jpc 6.0 Hz), 130.1 (s), 128.4 (t, Jpc 5.3 Hz), 13.3 (t, Jpc 19.6 Hz); mass spectrum (EI) 507 (M+). Anal. Calcd for C16H22BCl3P2Pt: H, 3.75; C, 32.65%. Found H, 3.85; C, 32.75%.

[PtCl(BCl2)(PMe3)][BCl4](5). [Pt(nbe)](0.10 g, 0.21 mmol) was dissolved inhexane (5 cm3), to which PMe3 (0.055 cm3, 0.42 mmol) was added through a micro-syringe. The reaction mixture was stirred for 1 h, and all the volatiles were removed in vacuo to give an off-white oil. The solid was redissolved in toluene (5 cm3), and an excess of BCl3 (0.4 cm3, 0.46 mmol, 1 M in heptane) was added at −78 °C. The mixture was allowed to warm to room temperature, and stirred for 1 h during which time a quantity of black oil formed. After this time, all volatiles were removed in vacuo, and the solution was cooled to −78 °C, to which NEt3 (0.5 cm3) was added followed by a solution of catechol (0.023 g, 0.21 mmol) in toluene (5 cm3). The mixture was stirred for 1 h, and the solid was then removed in vacuo, and the excess of NEt3 (0.5 cm3) was then added. The mixture was stirred overnight affording a white precipitate of compound 6 (0.043 g, 36.9%). Spectroscopic data for 6: NMR (CD,CN) 11B[H] δ 27.8 (br), 31P[H] δ −13.0 (Jref 2643 Hz), 1H δ 3.58−3.65 (q, 1.88 (t), 1.21 (br).

[PtCl(BCl(py))(PMe3)](7). A sample of compound 1 (0.10 g, 0.21 mmol) was dissolved in toluene (5 cm3) and the solution was layered with an excess of pyridine (3 cm3). After one week, a white precipitate of compound 7 was obtained which was washed with hexane (3 × 2 cm3) (0.052 g, 46.5%). Spectroscopic data for 7: NMR (CD, CN) 11B[H] δ 29.9 (Jref 961 Hz), 31P[H] δ −10.4 (Jref 2694 Hz). Both 6 and 7 are prone to loss of the Lewis base bound to boron which prevented more extensive spectroscopic and analytical characterisation.

[PtCl(BCl(NEt3))(PMe3)](8). A sample of compound 1 (0.10 g, 0.21 mmol) was dissolved in toluene (10 cm3), to which HNEt3 (0.085 cm3, 0.84 mmol) was added. After stirring for 2 h, the solution became cloudy and a white precipitate formed. The solution was filtered and allowed to stand overnight affording a precipitate of [NEt3]2PtCl. After filtration and removal of the solvent, compound 8 was obtained as a white solid (0.095 g, 91.7%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (0.5 cm3) layered with hexane. Spectroscopic data for 8: NMR (CDCl3) 11B[H] δ 35.9 (Jref 1028 Hz), 31P[H] δ −13.1 (Jref 2772 Hz), 1H δ 3.41−3.35 (q, 2H), 3.24−3.19 (q, 2H); 1.26 (t, 6H); 1.20 (Jref 3.0 Hz); 0.95 (t, 3H); 0.88 (t, 3H); 13C[1H] δ 47.5 (CH3); 41.3 (CH2); 22.1 Hz); 14.7 (s, CH3), 14.5 (m, Jref 19.1, Jref 38.2 Hz); mass spectrum (EI) 465(M+ − Cl). Anal. Calcd for C16H28BCl3NP2Pt: H, 5.65; C, 23.95%. Found H, 5.60; C, 24.00%.

[PtCl(BCl(pip))(PMe3)](9). A sample of compound 1 (0.10 g, 0.21 mmol) was dissolved in toluene (10 cm3), to which piperidine (0.081 cm3, 0.84 mmol) was added. After stirring for 2 h, the solution become cloudy and a white precipitate formed. The solution was filtered and allowed to stand overnight affording a precipitate of [pipH2]Cl. After filtration and removal of the solvent, compound 9 was obtained as a white solid (0.083 g, 78.3%). Spectroscopic data for 9: NMR (CDCl3) 11B[H] δ 34.3 (br), 31P[H] δ −9.9 (Jref 3000 Hz). Despite the similarity to compound 8, which has been fully characterised, satisfactory analytical data were not obtained for 9.

[PtCl(B(cat))(PMe3)](10). A sample of compound 1 (0.10 g, 0.21 mmol) was dissolved in toluene (5 cm3), and an excess of NEt3 (0.5 cm3) was added followed by a solution of catechol (0.023 g, 0.21 mmol) in toluene (5 cm3). The mixture was stirred for 2 h at room temperature affording compound 10 as a white solid (0.076 g, 72%). Spectroscopic data for 10: NMR (CD, CN) 11B[H] δ 33.3 (Jref 1039 Hz), 31P[H] δ −12.6 (Jref 2768 Hz), 1H δ 7.75−7.25 (m, CH3), 1.68−6.90 (m, C6H4), 1.14 (m, CH3), 13C[1H] δ 149.9 (s, C6H4); 121.7 (s, C6H4); 111.4 (s, C6H4); 14.8 (Jpc 2890 Hz); mass spectrum (EI) 383 (M+ − Cl). Anal. Calcd for C16H28BCl3P3Pt: H, 4.40; C, 28.75%. Found H, 4.30; C, 28.70%. Compound 10 was also prepared, although not isolated, by the following methods and identified spectroscopically (11B and 31P NMR).
Method (i). A sample of compound 8 (0.10 g, 0.19 mmol) was dissolved in toluene (5 cm³) to which a solution of catechol (0.063 g, 0.57 mmol) in toluene (5 cm³) was added.

Method (ii). A sample of compound 11 (0.11 g, 0.18 mmol) was dissolved in CH₂Cl₂ (1 cm³) and the solution was allowed to stand for 2 months. After this time, colourless crystals of 10 were obtained by layering the solution with hexane.

Method (iii). A sample of [Pt(PMe₃)₂(dppm)]Cl₂ was added. The resulting mixture was stirred for 2 h at room temperature to give white precipitate. The solvent volume was reduced to 1.5 cm³ in vacuo and the white precipitate was filtered off, washed with toluene (2 cm³) and hexane (2 × 2 cm³) and dried in vacuo (0.081 g, 65%). Colourless crystals suitable for X-ray crystallography were formed from solutions in CH₂Cl₂ (1 cm³) layered with hexane. Spectroscopic data for 11: NMR (CDCl₃) 13B¹[H] δ 49.4 (br), 31P¹[H] δ −14.3 (δfpp 1490 Hz), 1H δ 7.13–7.07 (m, C₆H₄, 4H), 6.91–6.86 (m, C₆H₄, 4H), 1.50 (br, CH₃, 18H), 12.08 (s, C₆H₄), 111.4 (s, C₆H₄), 19.2 (t, CH₃, δfpp 12.1); mass spectrum (EI) 346 (M + e).

Crystallographic data for compounds Ph₃BCl₃, PhMe₂PBCl₃, 3, 4 and Cl₂BP(Ph₃)CH₂(Ph₃)PBCl₃, were collected at 173 K on a Bruker-AXS SMART 1K diffractometer using Mo-Kα radiation (λ = 0.71073 Å). For compounds [Pt(μ-Cl)(μ-PMePh₂)₂][BCl₄], [PtCl₂(μ-Cl)(μ-Cl)(PCy₃)], 2 and 8, data were collected at 100 K on a Bruker-AXS SMART Apex diffractometer equipped with monochromator beam focusing optics using Mo-Kα radiation (λ = 0.71073 Å). For compounds [PtCl₂(PMe₃)₂][BCl₄], 10 and 11, data were collected using Cu-Kα radiation (λ = 1.5418 Å) at 100 K on a Bruker-AXS Proteum diffractometer equipped with a rotating anode source operated at 4.8 kW and Osnic CMF12-38Cu6 (blue) mirror optics. For all compounds, intensity data were collected as a series of frames, each of ω width 0.3°, integrated²⁸ and corrected for absorption²⁸ and solved and refined using routine techniques.²⁷ The symmetratically unique anion in complex [Pt(μ-Cl)(μ-PMePh₂)₂][BCl₄] shows positional disorder for three of its chloride atoms. A sensible model for this disorder was obtained by restraining the sets of Cl···Cl distances in each of the disordered components to be equal and restraining the displacement parameters of pairs of chlorine atoms opposite each other with respect to the undisordered B(1)–Cl(2)/axis to be equal. Attempts to find a satisfactory model for the solvent present in the structure of [Pt(PMe₃)₄(dpdm)Cl]Cl were unsuccessful and a diffuse solvent correction was applied to the intensity data of this compound using the SQUEEZE program of the Platon software suite.²⁸ The Flack parameter for [PtCl₂(PMe₃)₂][BCl₄] indicates that this crystal may be a racemic twin. Crystallographic data for all compounds are presented in Table 1. CCDC reference numbers 618559–618552.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612039n

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